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THEORETICAL STUDY OF (RS) - (4-BROMOPHENYL) (PYRIDINE-2YL) METHANOL USING DENSITY FUNCTIONAL THEORY

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ABSTRACT

At B3LYP/6-311+G (d, p) level, a theoretical study of (RS)-(4-bromophenyl) (pyridine-2yl) methanol was carried out using density functional theory (DFT). Calculation has also been made by theoretical IR and normal mode analysis of title compound. To understand the molecules' active sites, which are under study, the structure activity relationship based on the study of molecular electrostatic potential map of (RS)-(4-bromophenyl) (pyridine-2yl) methanol and frontier orbital gap was used.

KEYWORDS: Density Functional Theory, Vibrational Analysis, HOMO-LUMO & MESP

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Original Article

INTRODUCTION

The diphenyl methanols, RPh2COH, exhibit a very rich diversity of supra molecular arrangements, including isolated molecules, hydrogen-bonded dimers, trimers, tetramers and hexamers as well as continuous hydrogen-bonded chains [1]. It is therefore of considerable interest to investigate the influence of an addition potential acceptor of hydrogen bonds as achieved. The vibrational spectroscopic analysis is known to provide immensely invaluable molecular structure elucidation in synergy with quantum chemical calculations. In order to obtain a complete description of molecular dynamics, vibrational wave number calculations along with the normal mode analysis have been carried out at the DFT level employing the basis set 6-311+G(d, p). The optimized geometry of molecule under investigation and its molecular properties such as equilibrium energy, frontier orbital energy gap and molecular electrostatic potential energy map, have also been used to understand the properties and active sites of the molecule.

Within the framework of the density functional theory (DFT) [2], a quantum chemical study of the (RS)-(4-bromophenyl) (pyridine-2yl) methanol has been performed with Becke's three-parameter hybrid exchange functional [3] with Lee–Yang–Parr correlation functional (B3LYP) [4,5] and engaging 6-311 ++ G(d, p) basis set using the Gaussian 09 program package [6]. A scaling factor of 0.9679 has been applied [7, 8] as the DFT hybrid B3LYP functional appears to overestimate the fundamental normal modes of vibration. By combining the results of symmetry considerations, Gauss view 5 program [9] and the VEDA 4 program [10], the vibrational wave number assignment has been carried out. Figure 2 shows the calculation of IR spectra.

RESULT AND DISCUSSION

Molecular Geometry Optimization and Energies

For the calculation of the compound's molecular properties using DFT at the B3LYP level, with the

6311+G (d, p) basis set, the geometry of the title compound has been optimized. The optimized geometry of molecule (Figure 1) that is under study is confirmed to be located at the local true minima on potential energy surface, as the calculated vibrational spectra contains no imaginary wave number. The optimized structural parameters like bond angles, bond lengths and dihedral angles of title compound are shown in the Table 1. The (C - O) bond lengths 1.427 Å is seen to be close to the standard ester C - O bond lengths [11, 12]. These calculated bond angles and bond length are found to be in full agreement with those standard bond angles and bond lengths.

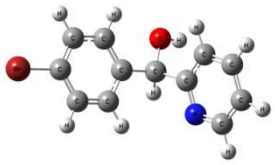

Figure 1: Optimized Geometry of (RS)-(4-Bromophenyl) (Pyridine-2yl) Methanol

Table 1: Optimize Parameters (Bond Length and Bond Angle) of (RS)-(4-Bromophenyl) (Pyridine-2yl) Methanol Calculated at B3LYP/6311+G (d, p) Level

Parameter	Bond Length (Å)	Parameter	Bond Angle (Degree)
C1-H2	1.0957	O3-C1-C5	108.3696
C1-O3	1.4272	O3-C1-C17	111.7021
C1-C5	1.5224	C5-C1-C17	111.3161
C1-C17	1.5281	C1-O3-H4	108.3242
O3-H4	0.9625	C1-C5-C6	121.5308
C5-C6	1.3951	C1-C5-C14	119.4787
C5-C14	1.3988	C6-C5-C14	118.9899
C6-H7	1.0819	C5-C6-H7	119.5374
C6-C8	1.3948	C5-C6-C8	120.67
C8-H9	1.0827	H7-C6-C8	119.7884
C8-C10	1.3891	C6-C8-H9	120.5581
C10-Cl11	1.7614	C6-C8-C10	119.3087
C10-C12	1.3919	H9-C8-C10	120.1328
C12-H13	1.0825	C8-C10-Cl11	119.5459
C12-C14	1.3912	C8-C10-C12	121.0331
C14-H15	1.0844	Cl11-C10-C12	119.4206
N16-C17	1.3374	C10-C12-H13	120.1997
N16-C24	1.3379	C10-C12-H14	119.0957
C17-C18	1.3982	H13-C12-C14	120.7044
C18-H19	1.0828	C5-C14-C12	120.9019
C18-C20	1.3897	C5-C14-H15	119.6989
C20-H21	1.0844	C12-C14-H15	119.3986
C20-C22	1.3935	C17-N16-C24	118.0385
C22-H23	1.0834	C1-C17-N16	115.9829
C22-C24	1.3915	C1-C17-C18	121.2471
C22-H25	1.0863	N16-C17-C18	122.7627
H2-C1-O3	110.4387	C17-C18-H19	119.8617
C18-C20-H21	120.437	H2-C1-C17-C18	158.2201
C18-C20-C22	118.9111	O3-C1-C17-N16	-143.4455

Table 1: Contd.,			
H21-C20-C22	120.6516	O3-C1-C17-C18	37.5135
C20-C22-H23	121.4195	C5-C1-C17-N16	95.263
C20-C22-C24	118.2013	C5-C1-C17-C18	-83.778
H23-C22-C24	120.3791	C1-C5-C6-H7	1.2869
N16-C24-C22	123.4441	C1-C5-C6-C8	-179.4635
N16-C24-H25	116.0027	C14-C5-C6-H7	-178.983
C22-C24-H25	120.5517	C14-C5-C6-C8	0.2666
H2-C1-O3-H4	-55.0146	C1-C5-C14-C12	179.4832
C5-C1-O3-H4	-173.6015	C1-C5-C14-H15	-0.2326
C17-C1-O3-H4	63.4141	C6-C5-C14-C12	-0.2525
H2-C1-C5-C6	-129.8172	C6-C5-C14-H15	-179.9683
H2-C1-C5-C14	50.454	C5-C6-C8-H9	-179.823
O3-C1-C5-C6	-9.9395	C5-C6-C8-C10	-0.0672
O3-C1-C5-C14	170.3317	H7-C6-C8-H9	-0.5753
H19-C18-C20-C22	179.8281	H9-C8-C10-Cl11	-0.1622
H19-C18-C20-C22	179.8281	H9-C8-C10-C12	179.6035
N16-C17-C18-C20	-0.0659	C8-C10-C12-H13	-179.6559
C17-C18-C20-H21	179.9832	C8-C10-C12-C14	0.1675

Vibrational Assignments

C_1 point group does not display any special symmetry and the optimized molecular structure belongs to this C_1 point group. Overestimation of the vibrational waver numbers in DFT methods and ab-initio are amended either by explicit computing anharmonic correlations or by presenting a scaled field, even directly scaling the deliberated wave numbers with proper factor.

Calibration of the vibrational wave numbers is done calibrated accordingly with the scaling factor of 0.9679 for DFT at B3LYP/6311+G (d, p) level. The vibrational assignments have been done on the basis of line shape, the VEDA 4 program, relative intensities and the animation option of Gauss view 5. Figure 2 shows the theoretical IR spectrum of the title compound. Table 2 represents the scaled calculated waver numbers along with their respective dominant modes.

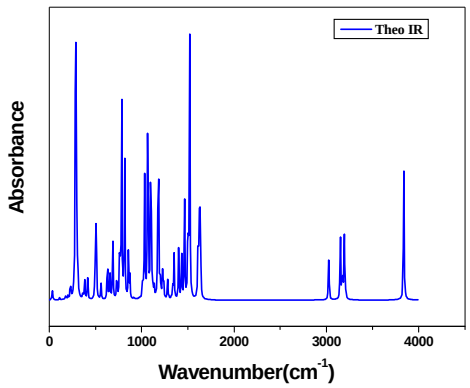

Figure 2: Theoretical IR Spectrum of (RS)-(4-Bromophenyl) (Pyridine-2yl) Methanol.

O-H Vibrations

The vibration of O-H stretching is very sensitive to hydrogen bonding. A non-hydrogen bonded hydroxyl group or a free hydroxyl group absorbs in the range 3700-3500 cm^{-1}. The hydroxyl stretching band is reduced to 3559-3200 cm^{-1} region by the intra-molecular hydrogen bonding present in the system [13]. The scaled wave number calculated at 3741

cm^{-1} is identified as O-H stretching with 100% contribution to P. E. D.

C-C and C-H Vibrations

It has been observed that C-C stretching wave numbers as mixed modes in the range 1100 cm^{-1} to 800 cm^{-1}. It appears that they agree well with the general appearance of C-H and C-C stretching modes. The C-C pure stretching is calculated to be 1583, 1575 and 1559 cm^{-1} which also support the previous studies. The vibration of (RS)-(4-bromophenyl) (pyridine-2yl) methanol's C-H stretching vibration has been observed in the range 3110-2929 cm^{-1}.

Ring Vibrations

The thiophene ring spectral region predominantly comprises the C–H, C–C, C-Cl, C-S and C=C stretching, and C–C–C as well as H–C–C-bending vibrations. The bands due to the ring C–H-stretching vibrations were observed as a group of partially overlapping absorptions in the region 3110–3069 cm^{-1} with more than 90% potential energy contribution. In the region 1600–825 cm^{-1}, vibrations involving C–H in-plane bending are found.

Table 2: Vibrational Analysis of Some Selected Modes of the Title Compound Calculated at the B3LYP/6311+G (d, p) Level

Calculated Freq.(cm^{-1})	Scaled Freq.(cm^{-1})	IR Intensity	Assignment
3838	3714	44.7	$\nu_{[(O3-H4)(100)]}$
3213	3110	1.4	$\nu_{[(C6-H7)(85)]}$
3200	3097	3.8	$\nu_{[(C18-H19)(76)]}$
3199	3096	2.1	$\nu_{[(C12-H13)(90)]}$
3193	3091	1.2	$\nu_{[(C8-H9)(85)]}$
3192	3090	14.9	$\nu_{as\ [(C18-H19)(16)+\ (C22-H23)(74)]}$
3175	3073	1.4	$\nu_{[(C14-H15)(90)]}$
3172	3070	7.4	$\nu_{[(C20-H21)(77)]}$
3151	3050	17.6	$\nu_{[(C24-H25)(93)]}$
3026	2929	13.7	$\nu_{[(C1-H2)(100)]}$
1635	1583	12.5	$\nu_{[(C14-C12)(30)]}$
1627	1575	37.7	$\nu_{as\ [(C18-C20)(25)+\ (C24-C22)(23)]}$
1611	1559	20.6	$\nu_{as\ [(N16-C17)(21)+\ (C22-C20)(18)]}$
1520	1471	71.0	$\sigma[(H9-C8-C10)(18)]+\ \sigma[(H13-C12-C14)(19)]$
1464	1417	26.7	$\sigma[(H21-C20-C22)(25)]+\ \sigma[(H23-C22-C24)(32)]$
1400	1355	13.8	$\sigma[(H4-O3-C1)(27)]+\ \sigma[(H2-C1-O3)(49)]$
1351	1308	13.1	$\sigma[(H25-C24-N16)(24)]+\ \tau_i\ [(H2-C1-O3-H4)(27)]$
1294	1252	0.8	$\nu_{[(N16-C24)(47)]}$
1237	1197	7.4	$\nu_{[(N16-C17)(19)]+}\ \nu_{[(C1-C17)(19)]}$
1181	1143	51.9	$\nu_{[(c5-C1)(19)]+}\ \sigma[(H4-O3-C1)(29)]$
1172	1134	6.1	$\sigma[(H19-C18-C20)(19)]+\ \sigma[(H21-C20-C21)(33)]+\ \sigma[(H23-C22-C24)(22)]$
1116	1080	4.5	$\sigma[(H23-C22-C24)(23)]$
1099	1064	52.5	$\nu_{[(C12-C10)(26)]+}\ \nu_{[(Cl11-C10)(18)]}$
1063	1029	34.9	$\nu_{[(O3-C1)(47)]}$
1031	998	36.2	$\sigma[(C10-C8-C6)(19)]+\ \sigma[(C12-C10-C8)(20)]+\ \sigma[(C14-C12-C10)(40)]$
1013	980	1.2	$\tau_i\ [(H21-C20-C22-C24)(39)]$
987	955	0.1	$\tau_i\ [(H7-C6-C8-C10)(30)]+\ \tau_i\ [(H9-C8-C10-C12)(21)]+\ \tau_i\ [(H15-C14-C12-C10)(18)]$
983	951	0.2	$\tau_i\ [(H25-C24-N16-C17)(52)]$
915	886	0.6	$\tau_i\ [(H19-C18-C20-C22)(45)]+\ \tau_i\ [(H23-C22-C24-N16)(20)]$
840	813	0.1	$\tau_i\ [(H7-C6-C8-C10)(19)]+\ \tau_i\ [(H9-C8-C10-C12)(29)]+\ \tau_i\ [(H13-C12-C14-C5)(30)]+\ \tau_i\ [(H15-C14-C12-C10)(19)]$

Table 2: Contd.,			
763	739	18.4	τ_i [(H23-C22-C24-N16)(27)]+ τ_i [(C17-N16-C24+C22)(23)]
732	708	7.9	τ_i [(C10-C8-C6-C5)(34)]
645	624	0.4	σ[(C10-C8-C6)(32)]+ σ[(C8-C6-C5)(20)]+ σ[(C14-C12-C10)(22)]
507	491	31.1	ν[(Cl11-C10)(26)]
414	401	6.5	τ_i [(C17-N16-C24-C22)(19)]+ τ_i [(C18-C20-C22+C24)(28)]
284	275	122.7	τ_i [(H4-O3-C1-C5)(76)]
228	221	5.1	σ[(C1-C17-N16)(37)]
178	172	1.1	σ[(C6-C5-C1)(44)]

Electronic Properties

Primarily acting electron donor is the highest occupied molecular orbital, HOMO. Similarly, the largely acting electron acceptor is the lowest unoccupied molecular orbital, LUMO. To characterize the kinetic stability and the chemical reactivity of the molecule, the frontier orbital energy gap is needed. Figure 3 and Figure 4 shows the 3D plots of the frontier orbital's HOMO, LUMO and the Molecular electrostatic potential map (MESP) respectively. The frontier orbital energy gap is found to be 5.302 eV.

The electrostatic potential is the energy of interaction of a positive test point charge with the nuclei and electrons of a molecule. The value of this potential mapped onto an electron iso-density surface may be engaged to differentiate the regions on the surface which are electron rich (subject to electrophilic attack) from those which are electron poor (subject to nucleophilic attack). Molecular electrostatic potential surfaces make clear that the structural similarity between two molecular does not carry over into their electrophilic/nucleophilic reactivity. Simultaneously, the resulting surface displays molecular shape, size and electrostatic potential in terms of colour grading. It is also a very useful tool that helps to investigate the correlation between the molecular structure and the physiochemical property relationship of molecules including bio molecules and drugs [14-21]. The difference in electrostatic potential created by a molecule is mainly responsible for the binding of a drug to its receptor binding sites. In general, the binding site is expected to have opposite areas of electrostatic potential. MESP plot of the title compound clearly shows that the potential swings wildly hydrogen atoms attach with oxygen atom and carbon, which bear most the brunt of positive charge (blue).

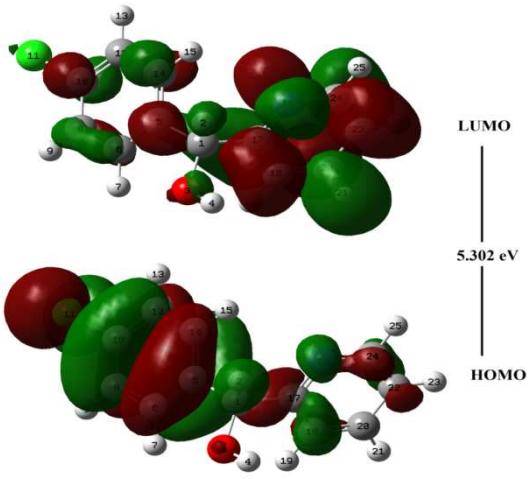

Figure 3: HOMO-LUMO Plots of (RS)-(4-Bromophenyl) (Pyridine-2yl) Methanol

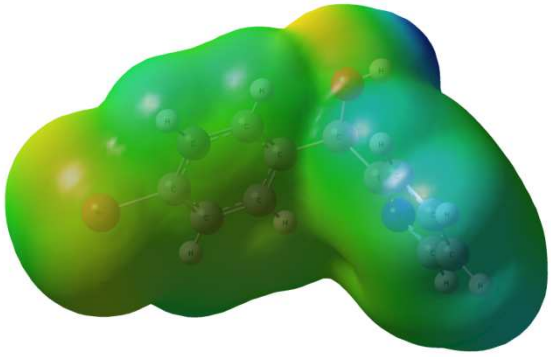

Figure 4: MESP Plot Of (RS)-(4-Bromophenyl) (Pyridine-2yl) Methanol

CONCLUSIONS

Using density functional theory, we have performed a detailed quantum chemical studies on (RS)-(4-bromophenyl) (pyridine-2yl) methanol at B3LYP/6311+G (d, p) level. Analysis on vibrational spectroscopy has been performed and prominent modes of vibration are assigned and discussed. The HOMO-LUMO gap provides a degree of charge transfer interaction. These observations may stimulate further interpretations on the biological activity of (RS)-(4-bromophenyl) (pyridine-2yl) methanol and related natural products.

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